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REMARKS

Claims 1, 2, and 4-24 are now of record in this application. Claims 1, 4, 5, and 8 have been amended, claim 3 has been cancelled, and new claims 22-24 have been added.

Support for the amendments is inherent in the original disclosure. Claim 1 has been amended to incorporate original claim 3 therein. Claims 4, 5, and 8 have been amended accordingly to correct their dependency. Support for new claim 22 may be found in paragraph no. 0027 on page 11. Support for new claims 23 and 24 may be found in paragraph no. 0026 on page 11 and Table 3 on page 20.

Rejection Under 35 U.S.C. 102/103

Claims 15-21 have been rejected under 35 U.S.C. 102(b) as being anticipated by, or in the alternative, as obvious over Bagreev in view of Shinogi (2003, Basic Characteristics of Low-Temperature Carbon Products from Waste Sludge, Adv. Environ. Res., 7:661-665) and Chiang. The Examiner has taken the position that the activated carbons of Bagreev contain a high phosphorous content (demonstrated by Shinogi) and anticipate the claims. Applicants respectfully disagree.

Bagreev discloses the production of adsorbent by the carbonization of municipal sewage sludge (i.e., Terrene). The

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sludge is pyrolyzed at 400 to 950°C in a nitrogen atmosphere and washed in HCl (page 1537, col. 2, under "Materials"). These adsorbents are designated SC400 through SC950, depending on the temperature of pyrolysis. The BET surface area of the adsorbents is shown in Table 4 on page 1541. The highest surface area is exhibited in CS800A, with a BET surface area of 193 m<sup>2</sup>/g. Note that samples designated "S208" refer to carbons produced from coconut shells (page 1537, col. 2, last paragraph). The authors also note that the adsorbents contained catalytically effective amounts of iron, copper and aluminum oxides (page 1540, col. 1, lines 1-3 of the last paragraph). The carbonized sewage sludge is effective as an adsorbent for hydrogen sulfide.

Shinogi (2003, Basic Characteristics of Low-Temperature Carbon Products from Waste Sludge, Adv. Environ. Res., 7:661-665) discloses the preparation of a pyrolysis product of cattle manure by heating to 380°C in an atmosphere of limited air, and reports the properties of the product. The pyrolysis product has a very low surface area of 2.2 m<sup>2</sup>/g, an ash content of 25.6% and an elemental carbon content of 49.2%. The authors describe the main use for the pyrolysis product as a soil amendment due to the high phosphate ion, organic nitrate and potassium ion content.

Chiang discloses the preparation of adsorbents by pyrolysis of municipal sludge. The sewage sludge is treated with ZnCl<sub>2</sub>,

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pyrolyzed by heating to 400 to 1,000°C in a N<sub>2</sub> atmosphere, and washed with HCL. The BET surface area is disclosed in Table 2 on page 924 and may be as high as 585.1 m<sup>2</sup>/g and varies with the temperature of pyrolysis and the ZnCl<sub>2</sub> concentration.

The instant invention is drawn to a process for the creation of activated carbon from poultry manure which possess enhanced activity for the adsorption of metal ions. The activated carbons of this invention are produced by carbonization (also known as pyrolysis) of the manure, followed by activation. Activation is effected by treatment of the pyrolyzed material with steam, CO<sub>2</sub> or other activation gas (paragraph no. 0022 bridging pages 8-9, and lines 14-22 of paragraph no. 0025 bridging pages 10-11). The resultant activated carbons produced from poultry manure possess a high BET surface area, at least about 200 m<sup>2</sup>/g, and exhibit high metal ion adsorption capabilities in comparison to conventional activated carbons. In addition, these activated carbons prepared from poultry manure have a high phosphate ion content, at least about 4% by weight, which applicants believe provides the above-mentioned ion adsorption capabilities. This is not disclosed or suggested by the prior art.

Neither the primary reference, Bagreev, nor the cited supporting references, Shinogi and Chiang, disclose or suggest producing activated carbons from poultry manure as claimed.

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Municipal sludge, which will typically comprise a diverse mixture of materials generated from homes, businesses and sewer runoffs ranging from human excrement to human foods, laundry wastewater, home and industrial chemicals, rainwater, fertilizers, pesticides, and soil, is far different from poultry manure, defined in the specification as containing bird droppings, feathers and bedding material (paragraph no. 0018, pages 6-7). Thus, this 102/103 rejection must be based upon a holding of inherency. However, Bagreev contains disclosures which unmistakably distinguish the pyrolytic adsorbent disclosed therein from that of the claimed invention. Of particular note, the adsorbent of Bagreev possesses a significantly lower surface area and it is not activated.

Bagreev discloses at Table 4 on page 1541 that the BET surface area varies from 8 to 193 m<sup>2</sup>/g. The highest surface area is exhibited in CS800A, with a BET surface area of 193 m<sup>2</sup>/g, below the claimed BET surface area of 200 m<sup>2</sup>/g, and significantly less than the area of 300 m<sup>2</sup>/g of claim 13. Further, the adsorbent of Bagreev is not activated, but only pyrolyzed. In other words it is simply a char. Activation to produce activated carbons, as claimed, requires the treatment of the pyrolytic product (i.e., char) with an activating gas such as steam to remove organic contaminants and increase pore size (lines 14-22

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of paragraph no. 0025 bridging pages 10-11). The prior art of record, confirms that the activation of a pyrolyzed char is generally recognized in the art to modify the char by effectively removing contaminants therefrom and increasing pore structure (see, for example, Abe, U.S. patent 5,338,462, col. 6, lines 33-42; and page 715, paragraph 3 of Bilitewski, Production and Possible Applications of Activated Carbon from Waste, Recycling Berlin, '79 Int. Recycling Cong. Thome-Kozimiensky, Ed, Berlin, V1, 1979, 714-721; each of which were supplied in the Disclosure Statement submitted September 10, 2007). Thus the pyrolyzed but not activated product or char of Bagreev would be expected to contain more contaminants and have a poor pore structure in comparison to the activated carbons of the instant invention.

In addition to the comments *supra*, applicants stress that activated carbons which are prepared from a different starting materials, such as sewage sludge, rather than poultry manure, would not possess the same properties, and particularly would not exhibit the same high capacity for metal ion adsorption, as activated carbons produced from poultry manures in accordance with applicants' invention. Again, the effect of the starting material on the properties of activated carbons, and particularly the difference in adsorption properties even among materials having similar high BET surface areas, is particularly apparent

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in Examples 2 and 3 of the instant specification wherein applicants compared a variety of activated carbons with those prepared from poultry manures. As shown in Tables 2 and 3, although other activated carbons also possessed equal or higher BET surface areas than those prepared from poultry manures, all were significantly less effective adsorbents for metal ions.

Specifically with respect to the properties of activated carbons produced from municipal sewage sludge, Fitzmorris et al. (2006, Journal of Residual Science & Technology, 3:161-167, a copy of which is enclosed and of which the instant applicants are co-authors) compared the effectiveness of activated carbons prepared from sewage sludge and poultry manure as adsorbents for various anions and cations. As summarized in Tables 1 and 2, activated carbons produced from poultry manure (litter or cake) exhibited significantly greater adsorption of the metal cations cadmium, chromium, copper, nickel, and zinc than activated carbons produced from sewage sludge.

Rejection Under 35 U.S.C. 102/103

Claims 15-21 have been rejected under 35 U.S.C. 102(b) as being anticipated by, or in the alternative, as obvious over Chen in view of Shinogi (Basic Characteristics of Low-Temperature Carbon Products from Waste Sludge, Adv. Environ. Res., 2003, 7,

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661-665) and Chiang. The Examiner has taken the position that the activated carbons of Chen contain a high phosphorous content (demonstrated by Shinogi) and anticipate the claims. Applicants respectfully disagree.

Chen discloses the production of pyrolyzed adsorbents from municipal sewage sludge for removal of pollutants. The reference discloses impregnating the sludge with zinc chloride prior to pyrolysis, and that the resultant adsorbent comprises a BET surface area of 647 m<sup>2</sup>/g. Additionally, the reference discloses that the adsorbent is effective for adsorption of phenol and carbon tetrachloride.

Shinogi, Chiang, and the instant invention were described in the response to the rejection over Bagreev.

As in the rejection over Bagreev, the adsorbent of Chen is not activated, but only pyrolyzed. Again, activation to produce activated carbons, as claimed, requires the treatment of the pyrolytic product (i.e., char) with an activating gas such as steam to remove organic contaminants and increase pore size. This is not disclosed by Chen, and thus the pyrolyzed but not activated product or char would be expected to contain more contaminants and have a lesser pore structure than an activated carbon such as in the instant invention.

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The adsorbent of Chen also differs from the activated carbon of the invention in its adsorbent properties. As with Bagreev, the adsorbent of Chen is also produced from municipal sewage waste, and thus would not possess the same properties, and particularly would not exhibit the same high capacity for metal ion adsorption, as activated carbons produced from poultry manures as claimed. Applicants arguments with respect to the adsorption properties of the materials presented in the response to the rejection over Bagreev are equally applicable here.

Rejection Under 35 U.S.C. 103

Claims 1, 2, 7, 9-13 and 15-20 have been rejected under 35 U.S.C. 103 as being unpatentable over Carugati in view of Landis and Shinogi (2003, Pyrolysis of Plant, Animal and Human Waste: Physical and Chemical Characterization of the Pyrolytic Products, Biosresource Technol., 90:241-247). The Examiner has taken the position that it would have been obvious to substitute the manure of Landis for the coal of Carugati as a source of humic acid for preparing activated charcoal. Applicants respectfully disagree.

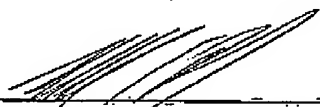
Applicants believe that their remarks presented in response to this rejection in the last Office action are still appropriate and are repeated. However, in an effort to expedite prosecution,

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claim 1 has been amended to insert the limitations of non-rejected claim 3 therein. Allowance is respectfully requested.

For the reasons stated above, claims 1, 2, and 4-24 are believed to distinguish over the prior art of record. Allowance thereof is respectfully requested.

Respectfully submitted,

  
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enclosure:

-Fitzmorris et al. 2006, Journal of Residual Science & Technology, 3:161-167 (7 pages).

# Anion and Cation Removal from Solution using Activated Carbons from Municipal Sludge and Poultry Manure

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**ABSTRACT:** The removal of potentially toxic metal cations and anions from water is essential to providing safe water for consumption and recreation. The objective of this study was to evaluate the ability of activated carbons made from municipal sludge and poultry manure to remove certain metal cations and anions from solution. Adsorption of the cations cadmium, copper, chromium, lead, nickel and zinc and the anions arsenic and selenium was carried out at pH 5. Lead was the most easily adsorbed cation by all three carbons, and the carbon from poultry cake adsorbed more cations, in general, than the other two carbons. However, arsenic and selenium were adsorbed more readily by the sludge-based carbon than the manure-based carbons. Combinations of both sludge- and poultry manure-based carbons may be efficacious toward the removal of low levels of cations and anions commonly found in municipal and industrial wastewater.

## INTRODUCTION

THE issue of removal of potentially toxic metal cations and anions including arsenic and selenium from diverse water sources has taken on greater importance over the last decade because of the documented link between their presence and adverse effects on human health. The metals lead, cadmium, nickel, zinc, chromium, and copper along with the non-metallic anions selenium and arsenic used in this study are listed as priority toxic pollutants by the National Recommended Water Quality Criteria developed by the US EPA (EPA, 1999) and are found on the 2003 CERCLA Priority List of Hazardous Substances (ATSDR, 2003).

The production of municipal sludge and animal manures is increasing yearly in the United States resulting in the need for new, innovative disposal solutions. The key to this problem is finding reuse options for the wastes that are valuable to the producer. The use of manures as fertilizer sources high in nitrogen and phosphorus is beneficial, but the production rates generally exceed the amount necessary for application and do not meet plant requirements. The agricultural community

is currently struggling to provide adequate treatment for manures due to the high cost of treatment processes and the restrictions on reuse.

In considering the reuse potential of the waste materials, activated carbon was chosen due to its high market value. Existing research into the use of municipal biosolids as a source for activated carbons is limited. Most of the work focuses on use as a fuel source (Inganzo et al., 2002) or in the pyrolysis of sludges without activation conditions applied (Bashkova et al., 2001; Bagreev and Bandoz, 2002). Bilitewski (1979) converted municipal biosolids and other waste materials to activated carbon. He used sewage sludge, municipal solid waste and poultry droppings along with waste tires and paper mill waste as sources for activated carbon. The municipal waste exhibited a BET (Brunauer Emmett Teller) surface area of 102.3 m<sup>2</sup>/g, second only to paper mill waste in his study. The poultry droppings had a lower percent ash (52.4%) than the sewage sludge (75–80%) although the BET surface area was 60.5 m<sup>2</sup>/g. Work that is more recent has investigated further the use of municipal waste as source for activated carbon. In studies such as those by Chiang and You (1987), Jeyaseelan and Qing (1996), Tay et al. (2001a and 2001b), Chen et al. (2002) and Martin et al. (1996), activation was conducted with ZnCl<sub>2</sub> and the adsorption of various organics was investigated. Rozada et al. (2003)

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and Martin et al. (2003) examined the adsorption of dyes using the carbons activated with  $H_2SO_4$ .

The use of poultry waste as a source of activated carbon (Bilitewski, 1979, Lima and Marshall, 2005a, 2005b, 2005c) is promising due to the high organic content of the litter and cake. Additionally, Lima and Marshall (2005a, 2005b) demonstrated that carbons from broiler cake and litter showed high adsorption potential towards the divalent cations of cadmium, copper, nickel and zinc. Combining this finding with the absence of commercial carbons on the market capable of adsorbing metals, greatly increases the potential of poultry waste carbons to fit into a much needed market niche. The key is the profitable reuse of wastes that currently do not represent much more than a liability for the producers.

The objective of this study was to determine the efficacy of cation and anion adsorption by carbons made from municipal sludge, poultry litter, and poultry cake. For the adsorption studies, several cations and anions were selected for a competitive study based on their importance as environmental contaminants. The concentrations of these ions were kept at a value where they are sometimes encountered in municipal and industrial wastewater. Two representative cations (lead, cadmium) and one representative anion (arsenic) were also evaluated on an individual basis to compare the adsorption with those results from the competitive study.

## MATERIALS AND METHODS

### Materials

The municipal sludge cake was obtained from the Morgan City Wastewater Treatment plant, Morgan City, LA where it was spread and dried indoors on plastic sheeting for ten days. The final moisture content of the sludge cake was 10 to 15%. Poultry litter and poultry cake were obtained from the USDA-ARS, Waste Management and Forage Research Unit, MS State, MS and, as collected, had a moisture content of 25 to 30%.

The metal cations, consisting of cadmium ( $Cd^{2+}$ ), chromium ( $Cr^{3+}$ ), copper ( $Cu^{2+}$ ), lead ( $Pb^{2+}$ ), nickel ( $Ni^{2+}$ ) and zinc ( $Zn^{2+}$ ) and non-metal anions, consisting of arsenic ( $As^{5+}$  as arsenate) and selenium ( $Se^{6+}$  as selenate) used in this study were obtained from Fisher Scientific in a SPEX CertiPrep Plasma Emissions Standard Kit (ICP-KIT-2).

### Drying and Pelletization

Municipal sludge cake, broiler litter and broiler cake were milled in a Retsch cross-beater mill (Glen Mills, Clifton, NJ) to a particle size of less than US 20 mesh (mm). At this stage, samples of sludge, broiler litter and cake were sent to an outside laboratory (Central Analytical Laboratories, Metairie, LA) for elemental analysis of total carbon, nitrogen, phosphorous and sulfur. The same laboratory also determined ash and moisture content. The remainder of the municipal sludge, broiler cake and litter was brought to a moisture level of 20 to 35% by mixing the dried samples with water in a ribbon blender. Moisture content was monitored by using a Sartorius Moisture Analyzer model MA 51 (Sartorius, Brentwood, NJ). The samples were pelletized in a PMCL5 Lab pellet mill (California Pellet Mill, Merrimack, NH) equipped with a 5 mm die plate. The pellets produced were cylindrical with a 5 mm diameter and 5 mm length.

### Pyrolysis and Activation

Pelletized sludge, broiler cake and litter were placed in a ceramic evaporating dish and then placed in a bench furnace equipped with a retort (Lindberg/Blue M, Watertown, WI). Pellets were pyrolyzed at 700°C for one hour under a flow of nitrogen gas set at a flow rate of 0.1 m<sup>3</sup>/h. Steam activation involved injecting water at a flow rate of 3 mL/min, using a peristaltic pump, into a flow of nitrogen gas entering the heated retort. Pyrolyzed chars were activated at 800°C for 45 min. The optimum activation conditions were determined from previous studies using copper adsorption rates and BET surface area analysis (Lima and Marshall, 2005a). Activated carbons were allowed to cool to room temperature overnight in the retort. The samples were then rinsed through a 250  $\mu$ m (60-mesh) sieve and stirred for one hour at 200 rpm in 0.1 mol/L HCl. The carbon was rinsed again through the 250  $\mu$ m sieve and placed in 3L of deionized water. This rinsing process was repeated three times. At that time, a small sample of the carbon was placed in a solution of 0.08 mol/L  $Pb(NO_3)_2$ . If precipitation occurred, the acid wash/rinsing process was repeated until no precipitate formed. The sample was then rinsed again, placed in a pre-weighed crystalline dish, and dried overnight at 80°C.

Prior to analysis, the carbon was ground and sieved to less than 45  $\mu$ m particle size to ensure a consistent prod-

uct. The carbon was analyzed in the powdered form to achieve faster uptake rates, and to eliminate the aspect of diffusion.

A sample of the dried carbons was sent to an outside laboratory for elemental analysis of total carbon, nitrogen, phosphorous and sulfur and also ash and moisture content.

### Physical Properties

Carbon yield was calculated by the following equation:

$$\text{Carbon yield (\%)} = [(W_t \div W_m) \times 100]$$

Where  $W_m$  = dry weight in g of the sludge or manure and  $W_t$  = dry weight in g of the carbon after acid and water washes.

Surface area measurements were taken using the NOVA 2000 Quantachrome Surface Area Analyzer (Model #N22-14, Boynton Beach, FL). BET surface area was obtained from nitrogen adsorption isotherms at 77°K. Micropore distributions were calculated using t-plots derived from the NOVA 2000 software.

A tamping procedure described by the American Water Works Association was used to determine the apparent bulk densities for the carbons. In this procedure a 10ml tube with sample was filled 1ml at a time, capping and tapping to a constant (minimum) volume. The apparent density ( $\text{g}/\text{cm}^3$ ) was calculated as the ratio between weight and volume of packed dry material. The method is adapted from ISO 787-11:1995. Attrition was not assessed since the carbons used were in a powder form of less than 45  $\mu\text{m}$  particle size for all adsorption studies.

The pH was monitored according to method 4500 H<sup>+</sup> of The Standard Methods for the Examination of Water and Wastewater (APHA, 1998).

### Adsorption Properties

Two separate sets of samples were required for this study. The first set designated as the control contained 25 mL of solution containing 10 mg/L of each of the eight cations and anions. The second set of samples contained the same solution of cations and anions along with the carbon. These experiments were designated "Competition study" due to the presence of all eight cations and anions. In a separate study, designated the "Individual ion study," the cations cadmium and lead

and the anion arsenic were evaluated individually with the same controls set up as before. The methodology was the same for both experiments. The carbons were assessed for their ability to adsorb metal ions and non-metal ions using solutions containing 10 mg/L of each cation or anion. A carbon dosage of 0.25 g was added to 25 mL of 10mg/L ion solution and the pH of both sets of samples was adjusted to 5 with either 0.1mol/L HCl or 0.1 mol/L NaOH. The individual ion study was also conducted at pH 5. This pH value was determined to be optimum from previous studies with relation to minimum precipitation and maximum adsorption (unpublished data). The ion mixture without carbon and the ion mixture with carbon were agitated with a magnetic stirrer at 300 rpm for 4h. The pH was adjusted during the course of the experiment and the final pH was usually within  $\pm 0.5$  pH units of the nominal values, but within  $\pm 0.2$  pH units of matched control samples at the same pH. The addition of the carbon resulted in the pH of the solution drifting to 7-9 at the beginning of the experiment but was quickly adjusted back to within the desired range in not only the set of samples with the carbon, but also the controls. Aliquots from both sets of samples were drawn off in a disposable syringe, and then filtered through a 0.22  $\mu\text{m}$  pore size filter (Millipore Corp., Bedford, MA) to remove any precipitate or carbon particles. The sample was diluted 1:100 by volume with 0.63 mol/L nitric acid ( $\text{HNO}_3$ , Ultrapure, ICP grade) and analyzed by inductively coupled plasma (ICP) spectrometry using a dual view, Leeman Labs Profile ICP-AES (Leeman Labs, Hudson, NH).

## RESULTS

### Sample Characterization

Select physical and chemical properties of the carbons used in this study are presented in Table 1. The percentages of carbon, nitrogen, phosphorus, and sulfur are given for both the starting material and the end-product carbon, in order to compare concentration or loss of the elements during the carbonization and activation process.

More total carbon was found in the poultry cake and litter than the municipal sludge. The municipal sludge also had the lowest level of total carbon in the activated carbon product as well. Nitrogen and sulfur content of the source materials were low and were similar to each other. As in the case of total carbon, there was a reduc-

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Table 1. Physical and chemical properties of carbons used in this study.

Property	Municipal Sludge	Poultry Litter	Poultry Cake
Yield (%) <sup>*</sup>	49.1	30.8	28.7
Bulk density (g/mL)	0.84	0.54	0.82
Total surface area (m <sup>2</sup> /g)	123	441	426
Micro-pore surface area (m <sup>2</sup> /g)	64	354	357
Carbon (%)	Raw	21.3	34.4
	Activated Carbon	34.1	25.8
Nitrogen (%)	Raw	3.87	3.26
	Activated Carbon	0.67	0.75
Phosphorus (%)	Raw	1.75	1.86
	Activated Carbon	4.14	4.89
Sulfur (%)	Raw	0.88	0.67
	Activated Carbon	0.59	0.64

<sup>\*</sup>Activated carbon yield prior to washing

tion in nitrogen content upon carbonization and activation. Volatilization of carbon and nitrogen combined with hydrogen and/or oxygen likely occurred. Sulfur content remained at similar levels in all samples after pyrolysis and activation. Phosphorus, however, increased during pyrolysis and activation. This increase in phosphorus was also much higher in the poultry cake carbon. Phosphorus does not appear to be volatilized during heating, which may signify that it is in an ionic form rather than in an elemental or non-ionic form more subject to volatilization.

The municipal sludge carbon gave the best percent yield (49%) among the three carbons. Bulk densities were similar for the municipal sludge and poultry cake carbons and lower for the poultry litter carbon. However, the surface area for the municipal sludge carbon was the lowest of the three carbons. The poultry carbons exhibited surface areas around 3.5 times that of the municipal sludge carbon (123 vs. 441 or 426 m<sup>2</sup>/g). These total surface areas are relatively low compared to commercial carbons, which are generally in the range of 500 - 1500 m<sup>2</sup>/g (Wagner and Jula, 1981). The low surface areas suggest chemisorption may be the main form of adsorption, i.e. the functional groups on the surface of the carbons are playing the main role in adsorption, not the porosity.

Generally, in order to assess the value of carbons to adsorb metal ions, their negative surface charge is determined. Nutshell-based carbons with high negative surface charge, especially those values that exceed 3.0 mmol of H<sup>+</sup> equivalent per g of carbon, adsorb high concentrations of metal ions (Toles et al., 1999). The total negative surface charge of the carbons used in this study ranged from 0.0 to 0.78 mmol H<sup>+</sup>eq/g carbon at pH 5 (Data not shown).

Johns et al. (1999) found that pecan shell-based carbons that had been steam activated, such as the carbons in this study, and commercial carbons with surface charge in the above range had poor metal ion adsorption of about 0.20 to 0.30 mmol of metal ion bound per gram of carbon.

### Competitive Ion Study

Competition among metal cations and arsenic and selenium anions for adsorption sites on the carbon surface were investigated at pH 5. As stated in the methodology, controls were conducted to simulate the conditions of the adsorption vessels including the variations in pH specifically with relation to the carbon addition.

The cations and anions were investigated for their ability to bind to the three different activated carbons. The percent adsorption data was obtained by using the amount in the control as the starting concentration to which the final concentration was compared. Carbon adsorption results for the competition study are found in Figure 1 and appear to depend on the carbon employed.

For the sludge-based carbon, the highest percent adsorption of any ion was lead with greater than 90% adsorbed. This adsorption value was similar to those for the two poultry manure-based carbons, which achieved 100% adsorption of lead at pH 5. Arsenic and selenium also showed considerable adsorption (65% and 56%, respectively) for the municipal sludge carbon, where as the adsorption levels of the broiler cake and broiler litter carbons was negligible (less than 4%). The percent cadmium (27%), chromium (88%), and nickel (2%) bound by the sludge-based carbon were considerably below comparable values of 81% and 74% for cad-

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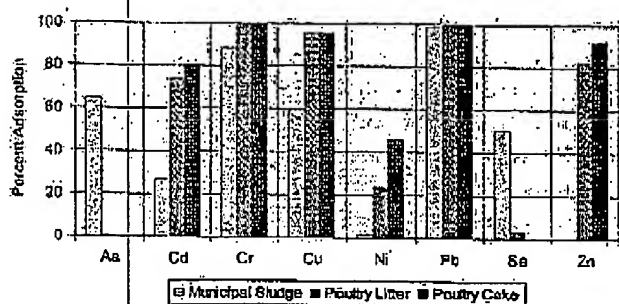


Figure 1. Percentage of anions and cations adsorbed by carbons made from municipal sludge, broiler cake and broiler litter in a competitive ion adsorption study.

mium, 100% and 100% for chromium and 46% and 24% for nickel for the broiler cake and broiler litter carbons, respectively.

Both broiler manure-based carbons adsorbed zinc in high amounts at pH 5 (> 80%) and have high chromium uptake (100%). In addition, the poultry cake carbon appeared to adsorb slightly higher levels of nickel than the poultry litter carbon, 46% versus 24%.

Overall, the manure-based carbons adsorbed significant amounts of the ions in solution and bound more cations than the sludge-based carbon.

### Individual Ion Study

The assessment of the adsorption of select cations and anions on an individual basis was conducted using the same experimental method as the "Competition study." The anion arsenic as arsenate and the metal ions cadmium and lead were selected out of the original eight ions because they showed good adsorption per-

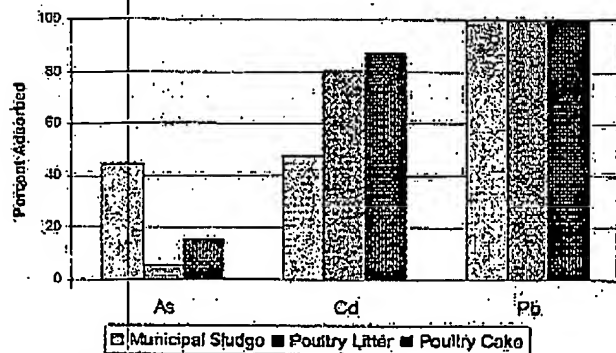


Figure 2. Percentage of arsenic, cadmium and lead adsorbed by carbons made from municipal sludge, broiler cake and broiler litter in an individual ion adsorption study.

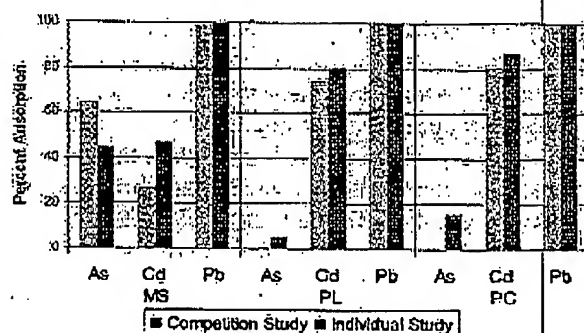


Figure 3. Comparison of percentages of anion and cation adsorption for arsenic, cadmium and lead based on their performance in the presence of competing ions or in the absence of competing ions.

centages with one or more of the carbons and also due to their importance as environmental pollutants.

A much greater percentage of arsenic (45%) was removed by the municipal sludge-based carbon than by the two broiler carbons (15% for cake and 6% for litter (Figure 2). This observation was similar to the results seen in the ion mixture (Figure 1) and reinforces the contention that the sludge-based carbon is better at arsenic removal. Removal of residual lead via adsorption was complete (100%) with all carbons examined. The broiler-based carbons removed a greater percentage of cadmium than the sludge-based carbon. The municipal sludge carbon adsorbed 47% and the poultry litter carbon and poultry cake carbon adsorbed 80% and 87%, respectively.

A comparison of percent adsorption of the cations cadmium and lead and the arsenate anion in the presence or absence of competing ions clearly demonstrates the strong adsorption of lead ion by all three carbons (Figure 3). Lead appears to be the ion of choice for removal and the presence of numerous cations and anions has little if any affect on its binding. Cadmium and arsenic display greater adsorption in the absence of competing ions except for arsenic binding to municipal sludge-based carbon.

### DISCUSSION

The levels of cations and anions used for adsorption purposes in these studies were established at 10 mg/L or 10 ppm to simulate values that can be found in various types of municipal and industrial wastewater. However, levels of chromium, copper, nickel and zinc can often exceed 10 mg/L in effluents found in the metal plating industry. For the present study, the carbons, in many cases, reduced the levels of the metals to below the

Maximum Contaminant Levels set forth in the US EPA Drinking Water Regulations (Pontius, 2003).

For carbon adsorption of anions (arsenic, selenium), the carbon produced from municipal sludge was found to bind a greater percentage of anion than the carbons made from poultry manure in both a competitive and individual ion situation. Overall, the poultry cake carbon performed the best out of the three carbons. As compared to the poultry litter carbon, the results were similar with regard to the type of metals adsorbed, though in general the poultry cake carbon adsorbed higher amounts. This phenomenon could be due to the composition of the waste itself. The main difference between poultry litter and poultry cake lies in the amount of bedding material to which the manure is added during a growout. The poultry litter includes a higher percentage of this bedding material (30% by volume) which is usually composed of wood shavings or other fibers high in cellulose. The poultry cake is limited to a maximum of 5% of bedding material. This is evident by the results in Table 1. The percent yield for the poultry litter was higher than the cake along with the carbon content, which indicates the presence of a higher level of plant-based material, in this case bedding.

The cations adsorbed most efficiently were lead, zinc, and chromium when these metal ions were available for carbon adsorption. At pH 5, both poultry carbons adsorbed zinc, and the municipal sludge carbon adsorbed chromium. In the individual ion study, the two poultry manure-based carbons poorly adsorbed arsenic. This could be due to the anionic properties of arsenic, which affects the charge relationship of the metal to the functional groups on the carbon, thus the surface properties of these carbons are such that they attract positively charged ions. Generally, the broiler manure-based carbons adsorbed more cations than the municipal sludge-based carbons.

In the case of arsenic and lead, the adsorption amounts were higher when the competition situation was removed. However, cadmium adsorption was comparable in the individual study and the competition study based on percent adsorbed for all three carbon types. In addition, the actual amounts adsorbed were lower in the competition study as compared to the individual study. This is evident by the percentages adsorbed staying consistent in the two studies, but the amount available for adsorption increasing in the individual study.

It is important to note the behavior of ionic species with regard to their classification. According to

Pearson's classification (Stumm and Morgan, 1996), nickel and copper are listed as borderline metals, though in the adsorption studies, they appeared to follow the behaviors of both the borderline and soft metals. The two most obviously similar metals are zinc and cadmium. It is easy to note from the adsorption values especially with the poultry carbons, the similarity in the adsorption of these two metals. At pH 5, zinc is predominantly occurring as  $Zn^{2+}$  and cadmium as  $Cd^{2+}$ . With the metals discussed above, it is interesting to note that the metal is adsorbed best in its ionized form.

It is also important to note from Pearson's classification that soft acids have an affinity for phosphorus as a ligand atom over nitrogen. This could be important with relation to the functional groups on the surface of the carbons responsible for adsorption. As noted in Table 1, phosphorus amounts increase when the raw material is converted to activated carbon. The metals in the borderline category may also show an affinity for phosphorous, but are not limited by them. Borderline metals may show preference for oxygen binding sites as would exist if the phosphorous is predominantly in the phosphate form (Stumm and Morgan, 1996).

## CONCLUSIONS

This study has shown that for anion adsorption, the carbon made from municipal sludge is effective in this regard and adsorbs a greater percentage of arsenic and selenium than two poultry manure-based carbons. On the other hand, for metal cation removal, the manure-based carbons are the better choice. Indeed, the two different types of carbons working together may be particularly effective in adsorbing many different anions and cations from solution at acidic pH values.

The adsorption of anions and cations is normally a function of the surface characteristics of the carbon. In the present case, the surface properties of the sludge- and manure-based carbons must be studied in detail to ascertain the functional groups responsible for their activity.

## DISCLAIMER

Mention of names of companies of commercial products is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the US Department of Agriculture over others not mentioned.

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